Enantioselective N-Heterocyclic Carbene-Catalyzed Cascade Reaction for the Synthesis of Pyrroloquinolines *via* N-H Functionalization of Indoles

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1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Dry DMSO was purchased from commercial sources and stored under argon over 4 Å molecular sieves. The α,β -unsaturated aldehydes **2a**, **2e**, **2f**, **2m**, **2t** were purchased from commercial sources and were used without further purification, and others were synthesized following the literature procedure.¹ Indole derivative **1d** were synthesized by following the literature procedure.² The triazolium salt **4** was synthesized following the literature procedure.³ 25 °C corresponds to the room temperature of the lab when the experiments were carried out.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F₂₅₄. Visualization was accomplished with short wave UV light or KMnO₄ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. ¹H and ¹³C NMR spectra were recorded on Bruker Ultrashield spectrometer in CDCl₃ or DMSO-*d*₆ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δ_{H} = 7.26 ppm, δ_{C} = 77.16 ppm and DMSO-*d*₆: δ_{H} = 2.50 ppm, δ_{C} = 39.50 ppm). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, ν -max in cm⁻¹. Optical rotations were measured on JASCO P-2000 polarimeter. HRMS (ESI) data were recorded on a Micromass Q-TOF Micro instrument. HPLC analysis was performed on Agilent Technologies 1260 Infinity II with UV detector.

¹ A. A. Wubea, A. Hüfner, C. Thomaschitz, M. Blunder, M. Kollroser, R. Bauer, F. Bucar, *Bioorg. Med. Chem.* **2011**, *19*, 567.

² Giardinetti, M.; Moreau, X.; Coeffard, V.; Greck, C. *Adv. Synth. Catal.* **2015**, *357*, 3501.

³ J. R. Struble, and J. W. Bode, *Org. Synth.* **2010**, *87*, 362.

2. General Procedure for the Optimization of Reaction Conditions^a

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (0.015 g, 0.0375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (0.125 mmol), and enal **2a** (0.125 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added solvent (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture base (0.125 mmol) was successively added. After 12 h, the reaction is quenched and the mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂ (10 mL). The solvent was removed to obtain the crude product, which was analyzed using ¹H NMR using CH₂Br₂ (9.0 μL, 0.125 mmol) as the internal standard. The enantiomeric ratio was determined by HPLC analysis on a chiral column.

Optimization Studies

Entry	(1)	Base	Solvent	Yield (%) ^b	dr ^c	er ^d
1	1a	DABCO	DMSO	<5	-nd-	-nd-
2	1b	DABCO	DMSO	<5	-nd-	-nd-
3	1c	DABCO	DMSO	42	>20:1	77:23
4	1d	DABCO	DMSO	60	>20:1	95:5
5	1d	DABCO	toluene	18	>20:1	56:44
6	1d	DABCO	CH ₂ Cl ₂	18	>20:1	70:30
7	1d	DABCO	THF	40	>20:1	73:27
8	1d	DABCO	DMF	61	>20:1	93:7
9	1d	DABCO	CHCl ₃	31	>20:1	75:25
10	1d	DABCO	EtOAc	36	>20:1	74:26
11	1d	DABCO	CH ₃ CN	69	>20:1	89:11
12	1d	DABCO	Acetone	52	>20:1	90:10
13	1d	DABCO	DME	18	>20:1	77:23
14	1d	DBU	DMSO	<5	-nd-	-nd-
15	1d	K ₂ CO ₃	DMSO	49	>20:1	95:5
16	1d	Cs ₂ CO ₃	DMSO	47	>20:1	95:5
17	1d	DMAP	DMSO	37	>20:1	95:5
18^d	1d	DABCO	DMSO	84	>20:1	95:5

^a Conditions: **1** (0.125 mmol), **2a** (0.125 mmol), **4** (10 mol%), **5** (1.0 equiv), base (1.0 equiv), solvent (1.0 mL), 25 °C and 12 h. ^b The yields were determined by ¹H NMR analysis of crude product using CH₂Br₂ as the internal standard. ^c Diastereomeric ratio was determined by ¹H NMR spectroscopy prior to purification. ^d Enantiomer ratio was determined by HPLC analysis on a chiral column. ^e 1.5 equiv each of **2a** and **5**, and 15 mol % of **4** was used.

The enhancement in reactivity and selectivity was observed while performing the reaction in polar aprotic solvents, such as CH₃CN, DMF, DMSO etc. To validate this, the reaction was performed in various solvents and the dielectric constant (DEC) of the solvent was plotted against the yield/ee of **3d** obtained (Figure S1).⁴ For instance, the reaction afforded poor yield/ee when performed in toluene (DEC: 2.38), moderate yield/ee in THF (DEC: 7.58), and high yield/ee in DMF (DEC: 36.7). Although a general linear relationship was not observed, the overall trend observed was that the reactivity/selectivity was improved in polar aprotic solvents.

Figure S1. Variation of yield/ee of **3d** with polarity of solvent (dielectric constant)

⁴ Gorman, W. G.; Hall, G. D. *J. Pharm. Sci.* **1964**, 53, 1017.

3. General Procedure for the Enantioselective Synthesis of Pyrroloquinolines

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (0.015 g, 0.037 mmol) and N-H indole derivative bearing a Michael acceptor moiety at the 7-position **1** (0.25 mmol), and enal **2** (0.375 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added DMSO (2.0 mL) under argon atmosphere. To this mixture DABCO (0.25 mmol) was successively added, and the resulting mixture was stirred at 25 °C for 12 h. When the reaction is complete, standard work-up of the reaction mixture was done using EtOAc and organic fractions were dried with Na₂SO₄, and solvent was evaporated. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding pyrroloquinoline derivatives **3**. All racemic pyrroloquinoline derivatives were prepared using NHC generated from the *N*-mesityl triazolium salt using DABCO.

Procedure for 1.0 mmol scale experiment

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **4** (56.0 mg, 0.15 mmol, 15 mol %) and N-H indole derivative bearing a Michael acceptor moiety at the 7-position **1d** (281.0 mg, 1.0 mmol, 1.0 equiv) and enal **2a** (198.0 mg, 1.5 mmol, 1.5 equiv) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added DMSO (8.0 mL) under argon atmosphere. To this mixture DABCO (112 mg, 1.0 mmol, 1.0 equiv) was successively added, and the resulting mixture was stirred at 25 °C for 12 h. When the reaction is complete, standard work-up of the reaction mixture was done using EtOAc and organic fractions were dried with Na₂SO₄, solvent was evaporated. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding pyrroloquinoline derivative **3d** as white solid (353 mg, 86% yield, >20:1 dr, 95:5 er).

4. X-ray Data of **3h**

Single crystal of **3h** (recrystallized from 1:4 CHCl₃/*n*-Hexane at 25 °C) was mounted and the diffraction data was collected at 296 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Kα radiation (71.073 pm). The structure was solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F². Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were

included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Identification code	3h
CCDC	CCDC 1863110
Empirical formula	C ₂₃ H ₁₅ ClF ₃ NO ₃
Formula weight	445.81
Temperature/K	296(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	10.3570(8)
b/Å	17.0723(13)
c/Å	23.2760(18)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	4115.6(5)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.439
μ/mm^{-1}	0.238
F(000)	1824.0
Crystal size/mm ³	0.25 × 0.15 × 0.12
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	5.768 to 55.19
Index ranges	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -30 ≤ l ≤ 30
Reflections collected	131106
Independent reflections	9493 [R _{int} = 0.0680, R _{sigma} = 0.0336]
Data/restraints/parameters	9493/0/561
Goodness-of-fit on F ²	1.031
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0489, wR ₂ = 0.1313
Final R indexes [all data]	R ₁ = 0.0803, wR ₂ = 0.1523
Largest diff. peak/hole / e Å ⁻³	0.34/-0.30
Flack parameter	0.00(2)

Figure S2. ORTEP representation of the X-ray structure of **3h** (thermal ellipsoids at 30% probability)

5. Synthesis and Characterization of Indole Derivatives

The *1H*-indole-7-carbaldehyde derivatives were prepared from following the known synthetic route depicted below.² Next, 3-(2,2,2-trifluoroacetyl)-*1H*-indole-7-carbaldehyde derivatives and 1-(triphenylphosphoranylidene)propan-2-one were added to CH₃CN. The reaction mixture was reflux for overnight. The reaction mixture cooled and the solvent was evaporated under reduced pressure. This was followed by purification using column chromatography to provide *N*-unsubstituted indole derivative bearing a Michael acceptor at the 7-position as a light green solid.

(*E*)-7-(3-Oxobut-1-en-1-yl)-1*H*-indole-3-carbaldehyde (1c)

Following the general procedure,² treatment of (*E*)-4-(1*H*-indol-7-yl)but-3-en-2-one (348 mg, 1.878 mmol) and phosphoryl trichloride (317 mg, 2.066 mmol) in DMF (2.0 mL) and stirring the reaction mixture at 25 °C for 16 h followed by flash column chromatography (Pet. ether- EtOAc: 7:3) to afford (*E*)-7-(3-oxobut-1-en-1-yl)-1*H*-indole-3-carbaldehyde **1c** as a white solid (151.0 mg, 37% yield).

R_f (Pet. ether /EtOAc = 70/30): 0.2;

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.68 (s, 1H), 10.02 (s, 1H), 8.47 (s, 1H), 8.23-8.17 (m, 2H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 16.2 Hz, 1H), 2.45 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 198.17, 185.22, 139.00, 137.88, 135.91, 128.01, 125.12, 123.28, 122.68, 121.67, 119.36, 118.40, 27.37. HRMS (ESI) calculated [M+H]⁺ for C₁₃H₁₂NO₂: 214.0863, found: 214.0868. FTIR (cm⁻¹) 3428, 2923, 2853, 2131, 1529, 1462, 1374, 1231, 1179, 990.

(*E*)-4-(3-(2,2,2-Trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one (1d)

Following the known procedure,⁵ 3-(2,2,2-trifluoroacetyl)-1*H*-indole-7-carbaldehyde (1.0 g, 4.14 mmol) and 1-(triphenylphosphoranylidene)propan-2-one (1.58 g, 4.9 mmol) were added to CH₃CN. The reaction mixture was reflux for overnight and concentrated followed by purified by column chromatography to provide (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one (**1d**) as a light green solid (0.91 g, 78% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.2; ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.18 (s, 1H), 8.59 (s, 1H), 8.26-8.19 (m, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 16.2 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 198.14, 174.11 (q, *J* = 34.3 Hz), 138.07 (q, *J* = 4.3 Hz), 137.27, 135.54, 128.53, 126.68, 123.89, 123.34, 122.04, 120.03, 116.78 (q, *J* = 290.0 Hz), 109.17, 27.34. HRMS (ESI) calculated [M+H]⁺ for C₁₄H₁₁O₂NF₃: 282.0736, found: 282.0745. FTIR (cm⁻¹) 3157, 2912, 1667, 1580, 1522, 1463, 1271, 1232, 1125, 956, 889.

(*E*)-1-Cyclopropyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one (1w)

Following the known procedure,⁵ 3-(2,2,2-trifluoroacetyl)-1*H*-indole-7-carbaldehyde (0.2 g, 0.82 mmol) and 1-cyclopropyl-2-(triphenylphosphoranylidene)ethanone (0.36 g, 1.0 mmol) were added to CH₃CN. The reaction mixture was reflux for over night and concentrated followed by purified by column chromatography to provide (*E*)-1-cyclopropyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one (**1w**) as a white solid (0.21 g, 83% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.4; ¹H NMR (400 MHz, CDCl₃) δ 10.84 (s, 1H), 8.48 (d, *J* = 7.9 Hz, 1H), 8.21 – 8.13 (m, 2H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 15.7 Hz, 1H), 2.28-2.25 (m, 1H), 1.24-1.12 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 201.36, 175.62 (q, *J* = 35.2 Hz), 136.97, 135.60, 135.20 (q, *J* = 5.2 Hz), 127.19, 126.76, 125.11, 124.24, 123.37, 119.68, 117.07 (q, *J* = 291.0 Hz), 111.32, 21.53, 12.33. HRMS (ESI) calculated [M+H]⁺ for C₁₆H₁₃O₂NF₃: 308.0893, found: 308.0895. FTIR (cm⁻¹) 3361, 2913, 1664, 1591, 1447, 1390, 1272, 1181, 1130, 973, 888.

(*E*)-5-Methyl-1-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)hex-1-en-3-one (1x)

Following the known procedure,⁵ treatment of 3-(2,2,2-trifluoroacetyl)-1*H*-indole-7-carbaldehyde (250 mg, 1.036 mmol) and 4-methyl-1-(triphenyl-15-phosphaneylidene)pentan-2-one (448 mg, 1.244 mmol) in acetonitrile (5.0 mL) and stirring the reaction mixture in reflux for 12 h, followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*E*)-5-methyl-1-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)hex-1-en-3-one **1x** as a green solid (291.0 mg, 87% yield).

R_f (Pet. ether /EtOAc = 90/10): 0.45; ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.20 (s, 1H), 8.58 (s, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 16.1 Hz, 1H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 16.1 Hz, 1H), 2.66 (d, *J* = 6.9 Hz, 2H), 2.16 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 199.75, 174.10 (q, *J* = 34.3 Hz), 137.96 (q, *J* = 4.89 Hz), 136.01, 135.58, 128.18, 126.69, 123.88, 123.29, 122.05, 120.12, 117.18, 109.16, 48.69,

⁵ Mukherjee, S.; Ghosh, A.; Marelli, U. K.; Biju, A. T. *Org. Lett.* **2018**, *20*, 2952.

24.53, 22.48. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{17}F_3NO_2$: 324.1206, found: 324.1209. **FTIR (cm⁻¹)** 3359, 2956, 1658, 1528, 1461, 1369, 1297, 1264, 1180, 1130, 976.

(*E*)-4-(5-Bromo-3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one (1y)

Following the known procedure,⁵ 5-bromo-3-(2,2,2-trifluoroacetyl)-1*H*-indole-7-carbaldehyde (0.44 g, 1.38 mmol) and 1-(triphenylphosphoranylidene)propan-2-one (0.52 g, 1.65 mmol) were added to CH_3CN . The reaction mixture was reflux for overnight and concentrated followed by purified by column chromatography to provide (*E*)-4-(5-bromo-3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one (**1y**) as a light

green solid (0.4 g, 80% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.35; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 13.31 (s, 1H), 8.60 (s, 1H), 8.29 (d, *J* = 1.7 Hz, 1H), 8.08 (d, *J* = 16.2 Hz, 1H), 7.93 (d, *J* = 1.6 Hz, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 2.40 (s, 3H). **¹³C NMR (100 MHz, DMSO-*d*₆)** δ 198.00, 174.07 (q, *J* = 35.1 Hz), 138.81 (q, *J* = 4.5 Hz), 135.46, 134.37, 129.75, 128.20, 124.86, 124.05, 121.94, 116.65, 116.60 (q, *J* = 292.0 Hz), 108.58, 27.60. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{10}O_2N_1F_3Br$: 359.9842, found: 359.9847. **FTIR (cm⁻¹)** 3398, 3135, 2912, 1662, 1589, 1516, 1451, 1356, 1124, 976, 869.

6. Synthesis and Characterization of Pyrroloquinoline Derivatives

(7*S*,7*aS*,11*aR*)-10-Methyl-8-oxo-7-phenyl-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4-carbaldehyde (3c)

Following the general procedure, treatment of cinnamaldehyde **2a** (37.0 mg, 35 μ L, 0.280 mmol) and (*E*)-7-(3-oxobut-1-en-1-yl)-1*H*-indole-3-carbaldehyde **1c** (40.0 mg, 0.187 mmol) with triazolium salt **4** (10.3 mg, 0.0280 mmol), oxidant **5** (114.4 mg, 0.280 mmol) and DABCO (20.9 mg, 0.187 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether-

EtOAc: 7:3) to afford (7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4-carbaldehyde **3c** as a brown solid (27.0 mg, 42% yield).

R_f (Pet. ether /EtOAc = 70/30): 0.30; er = 77:23, $[\alpha]_{\text{D}}^{25} = +118.7$ (c 0.2, CHCl₃). **HPLC** (Chiralpak AD, 80:20 Hexane / IPA, 1.0 mL/min) *Minor*: 11.6 min, *Major*: 13.6 min.

¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.78 (s, 1H), 7.33-7.31 (m, 4H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.82 (s, 1H), 6.30 (s, 1H), 5.64 (d, *J* = 6.7 Hz, 1H), 3.70 (t, *J* = 6.1 Hz, 1H), 3.37 (d, *J* = 6.3 Hz, 1H), 1.94 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 184.02, 166.66, 149.21, 138.36, 136.09, 133.00, 128.44, 127.77, 124.50, 122.87, 122.14, 120.09, 119.98, 119.92, 118.77, 101.17, 55.94, 44.85, 26.33, 17.76. **HRMS (ESI)** calculated $[M+H]^+$ for C₂₂H₁₈O₃N: 344.1281, found: 344.1290. **FTIR (cm⁻¹)** 3406, 3103, 2923, 2807, 1761, 1659, 1522, 1451, 1150, 1075, 935.

(7*S*,7*aS*,11*aR*)-10-Methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3d**)**

Following the general procedure, treatment of cinnamaldehyde **2a** (50.0 mg, 47 μ L, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc:

9:1) to afford (7*S*,7*aS*,11*aR*)-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3d** as a white solid (86.0 mg, 84% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.50; er = 95:5, $[\alpha]_{\text{D}}^{25} = +156.6$ (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 7.7 min, *Major*: 9.9 min.

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.40-7.33 (m, 4H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 4.0 Hz, 2H), 6.36 (s, 1H), 5.66 (d, *J* = 6.8 Hz, 1H), 3.71 (t, *J* = 6.1 Hz, 1H), 3.40 (d, *J* = 6.2 Hz, 1H), 1.95 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.35 (q, *J* = 35.1 Hz), 167.52, 150.41, 138.85, 136.08 (q, *J* = 4.8 Hz), 133.37, 129.52, 128.90, 125.32, 124.84, 121.64, 121.48, 121.39, 116.99 (q, *J* = 291.0 Hz), 111.22, 101.92, 57.26, 45.81, 27.11,

18.69. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{17}O_3N_1F_3$: 412.1155, found: 412.1161. **FTIR** (cm^{-1}) 3412, 2923, 1763, 1672, 1517, 1393, 1146, 1048, 906.

(7*S*,7*aS*,11*aR*)-7-(4-(Dimethylamino)phenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3e)

Following the general procedure, treatment of (*E*)-3-(4-(dimethylamino)phenyl)acrylaldehyde **2e** (66.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h

followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(4-(dimethylamino)phenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3a** as a black solid (70.0 mg, 63% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.40; er = 98:2, $[\alpha]_D^{25} = +276.1$ (c 0.1, $CHCl_3$). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 14.6 min, *Major*: 11.3 min.

1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, $J = 7.9$ Hz, 1H), 8.0 (s, 1H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.17 (d, $J = 7.2$ Hz, 1H), 6.72-6.65 (m, 4H), 6.23 (s, 1H), 5.64 (d, $J = 6.7$ Hz, 1H), 3.78 (t, $J = 6.3$ Hz, 1H), 3.34 (d, $J = 6.3$ Hz, 1H), 2.93 (s, 6H), 1.94 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.32 (q, $J = 35.6$ Hz), 167.76, 150.42, 150.25, 136.21 (q, $J = 5.3$ Hz), 133.46, 126.31, 124.88, 124.71, 121.51, 121.36, 118.47, 115.58, 112.93, 110.96, 102.11, 56.85, 45.99, 40.54, 27.30, 18.73. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{22}O_3N_2F_3$: 455.1577, found: 455.1586. **FTIR** (cm^{-1}) 3428, 1763, 1670, 1615, 1519, 1451, 1391, 1143, 1047, 905.

(7*S*,7*aS*,11*aR*)-7-(4-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3f)

Following the general procedure, treatment of (*E*)-3-(4-methoxyphenyl)acrylaldehyde **2f** (61.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0

mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(4-methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3f** as a white solid (93.0 mg, 84% yield).

R_f(Pet. ether /EtOAc = 80/20): 0.35; er = 98:2, [α]_D²⁵ = +159.6 (c 0.1, CHCl₃). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 12.7 min, *Major*: 14.0 min.

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 1.1 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.29 (s, 1H), 5.65 (d, *J* = 6.9 Hz, 1H), 3.76-3.72 (m, 4H), 3.37 (dd, *J*₁ = 6.4, *J*₂ = 2.2 Hz, 1H), 1.94 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.30 (q, *J* = 36.1 Hz), 167.57, 159.96, 150.33, 136.06 (q, *J* = 4.9 Hz), 133.34, 130.63, 126.61, 124.84, 121.60, 121.41, 117.0 (q, *J* = 290.0 Hz), 114.83, 111.10, 101.98, 56.77, 56.41, 45.87, 27.17, 18.66. **HRMS (ESI)** calculated [M+H]⁺ for C₂₄H₁₉O₄N₁F₃: 442.1261, found: 442.1267. **FTIR (cm⁻¹)** 3444, 2927, 1763, 1672, 1515, 1391, 1254, 1177, 1047, 906.

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*p*-tolyl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3g)

Following the general procedure, treatment of (*E*)-3-(*p*-tolyl)acrylaldehyde **2g** (54.8 mg, 0.375mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h

followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3g** as a brown solid (100.0 mg, 93% yield).

R_f(Pet. Ether /EtOAc = 80/20): 0.46; er = 96:4, [α]_D²⁵ = 138.88 (c 1.0, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 8.9 min, *Major*: 10.1 min.

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8 Hz, 2H), 6.32 (s, 1H), 5.66 (d, *J* = 7 Hz, 1H), 3.73 (t, *J* = 6.6 Hz, 1H), 3.39 (dd, *J*₁ = 6.4, *J*₂ = 2.0 Hz, 1H), 2.32 (s, 3H), 1.95 (s,

3H). **¹³C NMR (100 MHz, CDCl₃)** δ 174.31 (q, *J* = 35.1 Hz), 166.58, 149.36, 137.88, 135.09 (q, *J* = 4.9 Hz), 134.82, 132.28, 129.13, 124.25, 123.81(d, *J* = 3.5 Hz), 120.59, 120.42 (d, *J* = 2.0 Hz), 116.23 (q, *J* = 290.7 Hz), 110.12, 100.96, 56.06, 44.84, 26.13, 20.08, 17.68. **HRMS (ESI)** calculated [M+H]⁺ for C₂₄H₁₉O₃NF₃: 426.1312, found: 426.1313. **FTIR (cm⁻¹)** 3442, 3024, 2924, 1763, 1672, 1516, 1452, 1390, 1146, 1049, 906.

(7*S*,7*aS*,11*aR*)-7-(4-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3h)

Following the general procedure, treatment of (*E*)-3-(4-chlorophenyl)acrylaldehyde **2h** (63.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by

flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(4-chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3h** as a white solid (90.0 mg, 81% yield).

R_f(Pet. ether /EtOAc = 80/20): 0.45; er = 93:7, [α]_D²⁵ = +168.6 (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 11.0 min, *Major*: 12.6 min.

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.0 (s, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30-7.26 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 2H), 6.33 (s, 1H), 5.66 (d, *J* = 6.9 Hz, 1H), 3.69 (t, *J* = 6.4 Hz, 1H), 3.37 (d, *J* = 6.3 Hz, 1H), 1.94 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.36 (q, *J* = 35.5 Hz), 167.126, 150.50, 137.34, 135.83 (q, *J* = 5.0 Hz), 134.94, 133.17, 129.73, 126.80, 124.98, 124.84, 124.82, 121.77, 121.56, 121.16, 116.95 (q, *J* = 291.0 Hz), 111.37, 101.79, 56.72, 45.65, 27.07, 18.69. **HRMS (ESI)** calculated [M+H]⁺ for C₂₃H₁₆O₃N₁F₃Cl: 446.0765, found: 446.0772. **FTIR (cm⁻¹)** 3129, 2924, 1762, 1673, 1517, 1493, 1388, 1147, 1013, 906.

(7*S*,7*aS*,11*aR*)-7-(4-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3i)

Following the general procedure, treatment of (*E*)-3-(4-bromophenyl)acrylaldehyde **2i** (79.1 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(4-bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one **3i** as a brown solid (107.0 mg, 87% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.46; er = 93:7, [α]_D²⁵ = 159.40 (c 1.0, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 11.3 min, *Major*: 13.2 min.

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.31 (s, 1H), 5.66 (d, *J* = 7.0 Hz, 1H), 3.68 (t, *J* = 6.6 Hz, 1H), 3.35 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.1 Hz, 1H), 1.95 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 174.33 (q, *J* = 35.2 Hz), 166.23, 149.49, 136.86, 134.38, 132.14, 126.08, 123.98, 123.80, 121.98, 120.78, 120.55, 120.16, 115.93 (q, *J* = 290.88 Hz), 110.36, 100.77, 55.76, 44.57, 26.05, 17.70. **HRMS (ESI)** calculated [M+H]⁺ for C₂₃H₁₆BrF₃NO₃: 490.0260, found: 490.0267. **FTIR (cm⁻¹)** 3437, 3130, 3024, 2924, 1762, 1672, 1517, 1452, 1146, 1048, 905, 833.

(7*S*,7*aS*,11*aR*)-10-Methyl-4-(2,2,2-trifluoroacetyl)-7-(4-(trifluoromethyl)phenyl)-7*a*,11*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3j)

Following the general procedure, treatment of (*E*)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde **2j** (75.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford

(7*S*,7*aS*,11*aR*)-10-Methyl-4-(2,2,2-trifluoroacetyl)-7-(4-(trifluoromethyl)phenyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3j** as a white solid (108.0 mg, 90% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.45; er = 92:8, $[\alpha]_D^{25} = +130.7$ (c 0.1, CHCl₃). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 8.7 min, *Major*: 11.6 min.

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 1.4 Hz, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.39 (t, J = 7.7 Hz, 1H), 7.20 (d, J = 7.4 Hz, 1H), 6.96 (d, J = 8.1 Hz, 2H), 6.44 (s, 1H), 5.68 (d, J = 7.0 Hz, 1H), 3.67 (t, J = 6.6 Hz, 1H), 3.43 (dd, J_1 = 6.4 Hz, J_2 = 1.9 Hz, 1H), 1.95 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.42 (q, J = 34.9 Hz), 167.14, 150.62, 142.86, 135.76 (q, J = 5.0 Hz), 133.16, 131.29 (q, J = 33.1 Hz), 126.59 (q, J = 3.8 Hz), 125.95, 125.09, 124.85, 122.36, 121.89, 121.66, 121.11, 116.95 (q, J = 292.0 Hz), 111.53, 101.70, 56.95, 45.57, 27.07, 18.68. **HRMS (ESI)** calculated $[M+H]^+$ for C₂₄H₁₆O₃N₁F₆: 480.1029, found: 480.1039. **FTIR (cm⁻¹)** 3445, 2926, 1763, 1674, 1518, 1452, 1390, 1326, 1147, 1015, 906.

Methyl 4-((7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*, 8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-7-yl)benzoate (3k**)**

Following the general procedure, treatment of methyl (*E*)-4-(3-oxoprop-1-en-1-yl)benzoate **2k** (95mg, 0.5mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375mmol) and DABCO (28.0 mg, 0.25mmol) in DMSO (2.0 mL) and stirring the reaction mixture

at 25 °C for 12h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford methyl 4-((7*S*,7*aS*,11*aR*)-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3k** as a black solid (84.5 mg, 72% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.42; er = 87:13, $[\alpha]_D^{25} = 121.28$ (c 1.0, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 18.4 min, *Major*: 20.4 min.

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 8.0 Hz, 1H), 7.99 (t, J = 7.97 Hz, 3H), 7.38 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H), 6.89 (d, J = 8.1 Hz, 2H), 6.41 (s, 1H), 5.66 (d, J = 6.7 Hz, 1H), 3.89 (s, 3H), 3.65 (s, 1H), 3.42 (d, J = 5.9 Hz, 1H), 1.94 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.39 (q, J = 35.2 Hz), 167.20, 166.23, 150.54, 143.66, 135.85 (q, J = 5.0 Hz),

133.18, 130.86, 130.78, 125.51, 125.01, 124.84, 121.79, 121.63, 121.12, 116.94 (q, $J = 291$ Hz), 111.44, 101.76, 57.07, 52.46, 45.57, 27.10, 18.72. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{17}O_3N_1F_3$: 412.1155, found: 412.1161. **FTIR (cm⁻¹)** 3441, 3023, 2954, 1763, 1722, 1672, 1518, 1390, 1285, 1146, 906.

(7*S*,7*aS*,11*aR*)-7-(3-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3l)

Following the general procedure, treatment of (*E*)-3-(3-bromophenyl)acrylaldehyde **2l** (79.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(3-bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3l** as a white solid (112.0 mg, 91% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.45; er = 95:5, $[\alpha]_D^{25} = +152.7$ (c 0.1, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 9.3 min, *Major*: 10.1 min.

¹H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, $J = 7.9$ Hz, 1H), 8.01 (s, 1H), 7.46 (d, $J = 7.9$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.19-7.15 (m, 2H), 7.10 (s, 1H), 6.64 (d, $J = 7.7$ Hz, 1H), 6.33 (s, 1H), 5.67 (d, $J = 7.0$ Hz, 1H), 3.70 (t, $J = 6.4$ Hz, 1H), 3.40 (d, $J = 6.3$ Hz, 1H), 1.94 (s, 3H). **¹³C NMR (100 MHz, $CDCl_3$)** δ 175.37 (q, $J = 35.3$ Hz), 167.19, 150.53, 141.17, 135.80, 133.12, 132.15, 131.12, 128.53, 124.98, 124.80, 123.99, 123.67, 121.81, 121.60, 121.10, 116.94 (q, $J = 291.0$ Hz), 111.45, 101.77, 56.68, 45.66, 27.04, 18.70. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{16}O_3N_1F_3Br$: 490.0260, found: 490.0265. **FTIR (cm⁻¹)** 3440, 2924, 1762, 1672, 1517, 1389, 1147, 1048, 1015, 906.

(7*S*,7*aS*,11*aR*)-7-(2-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3m)

Following the general procedure, treatment of 2-methoxy cinnamaldehyde **2m** (121.6 mg, 0.75 mmol) and (*E*)-4-(3-(2,2,2-

trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (140.6 mg, 0.5 mmol) with triazolium salt **4** (27.6 mg, 0.075 mmol), oxidant **5** (306.0 mg, 0.75 mmol) and DABCO (56.0 mg, 0.5 mmol) in DMSO (4.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(2-methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one **3m** as a yellow solid (200.0 mg, 90% yield).

R_f(Pet. ether /EtOAc = 80/20): 0.42; er = 98:2, $[\alpha]_D^{25}$ = 181.52 (c 1.0, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 5.5 min, *Major*: 7.8 min.

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.32-7.28 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 6.01 (d, *J* = 7.5 Hz, 1H), 5.65 (d, *J* = 6.9 Hz, 1H), 3.94 (s, 3H) 3.65-3.58 (m, 2H) 1.95 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 174.35 (q, *J* = 35.1 Hz), 166.85, 154.26, 149.42, 135.17 (q, *J* = 4.9 Hz), 132.75, 129.03, 127.44, 125.79, 125.01, 123.82, 120.60, 120.50, 120.41, 120.26, 116.05 (q, *J* = 290.9 Hz), 110.14, 109.85, 100.98, 54.71, 51

.97, 41.83, 26.50, 17.76. **HRMS (ESI)** calculated $[M+H]^+$ for C₂₄H₁₉F₃NO₄: 442.1261, found: 442.1265. **FTIR (cm⁻¹)** 3130, 3022, 2961, 1763, 1672, 1597, 1518, 1458, 1391, 1145, 906.

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*o*-tolyl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3n)

Following the general procedure, treatment of (*E*)-3-(*o*-tolyl)acrylaldehyde **2n** (55.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-10-methyl-7-(*o*-tolyl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3n** as a white solid (98.0 mg, 92% yield).

R_f(Pet. ether /EtOAc = 80/20): 0.50; er = 96:4, $[\alpha]_D^{25}$ = +263.2 (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 5.0 min, *Major*: 6.0 min.

¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.30-7.19 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.56 (s, 1H), 6.14 (d, *J* = 7.7 Hz, 1H), 5.68 (d, *J* = 7.0 Hz, 1H), 3.73 (t, *J* = 6.5 Hz, 1H), 3.29 (d, *J* = 6.3 Hz, 1H), 2.52 (s, 3H), 1.96 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.37 (q, *J* = 35.4 Hz), 167.57, 150.43, 136.94, 136.06 (q, *J* = 5.1 Hz), 133.83, 133.78, 131.57, 128.83, 127.15, 125.14, 124.83, 124.72, 121.54, 121.23, 116.98 (q, *J* = 291.0 Hz), 111.27, 102.00, 54.53, 43.55, 27.10, 19.00, 18.73. **HRMS (ESI)** calculated [M+H]⁺ for C₂₄H₁₉O₃N₁F₃: 426.1312, found: 426.1317. **FTIR (cm⁻¹)** 3424, 1759, 1671, 1517, 1454, 1397, 1346, 1145, 907.

(7*S*,7*aS*,11*aR*)-7-(2-Fluorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3o)

Following the general procedure, treatment of (*E*)-3-(2-fluorophenyl)acrylaldehyde **2o** (56.0 mg, 0.375mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375mmol) and DABCO (28.0 mg, 0.25mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12h followed by flash column

chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(2-fluorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8 (11*aH*)-one **3o** as a white solid (79.0 mg, 74% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.40; er = 93:7, [α]_D²⁵ = +130.2 (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 6.7 min, *Major*: 8.0 min.

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.01 (s, 1H), 7.40-7.31 (m, 2H), 7.20-7.15 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 6.12 (t, *J* = 7.5 Hz, 1H), 5.67 (d, *J* = 6.8 Hz, 1H), 3.67 (t, *J* = 6.4 Hz, 1H), 3.51-3.49 (m, 1H), 1.95 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.40 (q, *J* = 35.2 Hz), 167.12, 158.83 (d, *J* = 247.0 Hz), 150.61, 135.83 (q, *J* = 4.9 Hz), 133.43, 130.78 (d, *J* = 8.1 Hz), 126.84 (d, *J* = 3.0 Hz), 126.10, 125.97, 125.25 (d, *J* = 3.0 Hz), 125.01, 124.84, 121.75, 121.62, 121.19, 116.97 (q, *J* = 291.0 Hz), 116.34, 116.13, 111.42, 101.74, 52.13 (d, *J* = 3.2 Hz), 43.69, 27.40, 18.76. **HRMS (ESI)** calculated [M+H]⁺ for C₂₃H₁₆O₃N₁F₄: 430.1061, found: 430.1065. **FTIR (cm⁻¹)** 2925, 2125, 1763, 1673, 1519, 1454, 1394, 1147, 1048, 907.

(7*S*,7*aS*,11*aR*)-7-(2-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3p)

Following the general procedure, treatment of (*E*)-3-(2-chlorophenyl)acrylaldehyde **2p** (63.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column

chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(2-chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3p** as a white solid (106.0 mg, 95% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.50; er = 94:6, $[\alpha]_D^{25} = +213.4$ (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 5.2 min, *Major*: 6.2 min.

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.0 Hz, 1H), 8.01 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.31-7.26 (m, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.73 (s, 1H), 6.76 (d, *J* = 8.1 Hz, 2H), 6.33 (s, 1H), 6.14 (d, *J* = 7.7 Hz, 1H), 5.68 (d, *J* = 6.8 Hz, 1H), 3.64 (t, *J* = 6.3 Hz, 1H), 3.57 (d, *J* = 6.4 Hz, 1H), 1.95 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.36 (q, *J* = 35.4 Hz), 167.17, 150.59, 136.12, 135.88, 133.53, 131.26, 130.56, 130.25, 127.96, 126.83, 124.98, 124.71, 121.72, 121.53, 121.24, 116.92 (q, *J* = 291.0 Hz), 111.47, 101.68, 77.48, 77.16, 76.84, 54.95, 54.91, 42.84, 27.20, 18.72, 18.70. **HRMS (ESI)** calculated $[M+H]^+$ for C₂₃H₁₆O₃N₁F₃Cl: 446.0765, found: 446.0771. **FTIR (cm⁻¹)** 3440, 2959, 1762, 1675, 1518, 1447, 1391, 1147, 1042, 907.

(7*S*,7*aS*,11*aR*)-7-(3,4-Dichlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3q)

Following the general procedure, treatment of (*E*)-3-(3,4-dichlorophenyl)acrylaldehyde **2q** (75.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by

flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(3,4-dichlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3q** as a white solid (100.0 mg, 83% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.50; er = 93:7, $[\alpha]_{\text{D}}^{25} = +149.5$ (c 0.1, CHCl₃). **HPLC** (Chiralpak IB, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 12.2 min, *Major*: 13.8 min.

¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H), 7.40-7.36 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.01 (s, 1H), 6.58 (d, *J* = 8.3 Hz, 1H), 6.32 (s, 1H), 5.67 (d, *J* = 7.0 Hz, 1H), 3.69 (t, *J* = 6.3 Hz, 1H), 3.37 (d, *J* = 6.3 Hz, 1H), 1.94 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.40 (q, *J* = 35.2 Hz), 167.0, 150.61, 139.09, 135.64 (q, *J* = 4.9 Hz), 133.96, 133.36, 133.0, 131.56, 127.52, 125.09, 124.84, 124.75, 121.92, 121.68, 120.96, 116.91 (q, *J* = 291.0 Hz), 111.58, 101.68, 56.36, 45.54, 27.07, 18.69. **HRMS (ESI)** calculated $[M+H]^+$ for C₂₃H₁₅O₃N₁F₃Cl₂: 480.0376, found: 480.0380. **FTIR (cm⁻¹)** 3430, 2924, 1764, 1673, 1518, 1146, 1049, 907.

(7*S*,7*aS*,11*aR*)-7-(Benzo[d][1,3]dioxol-5-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3r**)**

Following the general procedure, treatment of (*E*)-3-(benzo[d][1,3]dioxol-4-yl)acrylaldehyde **2r** (66.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h

followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(benzo[d][1,3]dioxol-5-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3r** as a white solid (94.0 mg, 82% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.40; er = 97:3, $[\alpha]_{\text{D}}^{25} = +186.92$ (c 0.1, CHCl₃). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 16.9 min, *Major*: 18.8 min.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.29-6.23 (m, 3H), 5.93 (s, 2H), 5.66 (d, *J* = 6.8 Hz, 1H), 3.76 (t, *J* = 6.3 Hz, 1H), 3.34 (d, *J* = 6.3 Hz, 1H), 1.94 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.35 (q, *J* = 35.1 Hz), 167.47, 150.38, 148.73, 148.11, 135.97 (q, *J* = 5.0 Hz),

133.25, 132.53, 124.83, 124.80, 121.65, 121.47, 121.26, 118.94, 116.98 (q, $J = 290.0$ Hz), 111.21, 108.98, 105.83, 101.93, 101.66, 56.97, 45.90, 27.21, 18.67. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{17}O_5N_1F_3$: 456.1053, found: 456.1056. **FTIR (cm⁻¹)** 3499, 3022, 1761, 1672, 1516, 1446, 1395, 1147, 1042, 862.

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(naphthalen-2-yl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*s*)

Following the general procedure, treatment of (*E*)-3-(naphthalen-2-yl)acrylaldehyde **2s** (68.3 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (13.8 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc:

9:1) to afford (7*S*,7*aS*,11*aR*)-10-methyl-7-(naphthalen-2-yl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one **3s** as a brown solid (88.0 mg, 77% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.42; er = 95:5, $[\alpha]_D^{25} = 166.48$ (c 1.0, $CHCl_3$). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 18.8 min, *Major*: 20.5 min.

¹H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, $J = 7.8$ Hz, 1H), 8.08 (s, 1H), 7.85 (t, $J = 7.5$ Hz, 2H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.49 (m, 2H), 7.41 (t, $J = 7.7$ Hz, 1H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.10 (d, $J = 10.1$ Hz, 2H), 6.53 (s, 1H), 5.64 (d, $J = 6.9$ Hz, 1H), 3.74 (t, $J = 6.4$ Hz, 1H), 3.52 (d, $J = 6.3$ Hz, 1H), 1.96 (s, 3H). **¹³C NMR (100 MHz, $CDCl_3$)** δ 174.44 (q, $J = 35.19$ Hz), 166.51, 149.45, 135.17, 132.43, 132.23, 132.20, 128.72, 127.06, 126.85, 126.14, 126.01, 123.90, 123.59, 121.74, 120.71, 121.72, 120.56, 120.40, 120.34, 116.0 (q, $J = 290.92$ Hz), 110.33, 100.93, 56.42, 44.77, 26.23, 17.72. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{27}H_{19}O_3NF_3$: 462.1312, found: 462.1316. **FTIR (cm⁻¹)** 3127, 3057, 2924, 1762, 1672, 1516, 1452, 1146, 1049, 906.

(7*S*,7*aS*,11*aR*)-7-(Furan-2-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*t*)

Following the general procedure, treatment of (*E*)-3-(furan-2-yl)acrylaldehyde **2t** (46.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-7-(furan-2-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3t** as a white solid (67.0 mg, 67% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.40; er = 96:4, $[\alpha]_{\text{D}}^{25} = +152.7$ (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 8.0 min, *Major*: 9.5 min.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 1.4 Hz, 1H), 7.38 (d, *J* = 1.2 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.34 (s, 1H), 6.30 (dd, *J*₁ = 3.2 Hz, *J*₂ = 1.9 Hz, 1H), 5.95 (d, *J* = 3.2 Hz, 1H), 5.72 (d, *J* = 7.0 Hz, 1H), 3.99 (t, *J* = 6.7 Hz, 1H), 3.68 (dd, *J*₁ = 6.6 Hz, *J*₂ = 2.1 Hz, 1H), 1.96 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.36 (q, *J* = 35.3 Hz), 167.06, 150.44, 150.41, 143.63, 135.93 (q, *J* = 5.0 Hz), 132.65, 124.92, 124.83, 121.55, 121.38, 120.98, 115.50 (q, *J* = 290.0 Hz), 111.23, 110.83, 108.24, 101.88, 51.85, 42.63, 28.25, 18.75. **HRMS (ESI)** calculated $[M+H]^+$ for C₂₃H₁₇O₃N₁F₃: 402.0948, found: 402.0951. **FTIR (cm⁻¹)** 2926, 1762, 1669, 1517, 1389, 1286, 1147, 1046, 996.

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(thiophen-2-yl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*u*)

Following the general procedure, treatment of (*E*)-3-(thiophen-2-yl)acrylaldehyde **2u** (52.0 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-10-methyl-7-(thiophen-2-yl)-

4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-8(11a*H*)-one **3u** as a white solid (84.0 mg, 81% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.40; er = 90:10, [α]_D²⁵ = +150.1 (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 9.0 min, *Major*: 11.9 min.

¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.9 Hz, 1H), 8.09 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 4.4 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.91 (s, 1H), 6.56 (s, 2H), 5.71 (d, *J* = 6.8 Hz, 1H), 3.94 (t, *J* = 6.3 Hz, 1H), 3.51 (d, *J* = 6.1 Hz, 1H), 1.95 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.36 (q, *J* = 35.1 Hz), 167.00, 150.40, 141.27, 135.90, 135.85, 132.58, 127.60, 126.11, 125.38, 124.92, 121.66, 121.45, 121.25, 120.92, 116.98 (q, *J* = 291.0 Hz), 111.26, 101.87, 53.76, 45.87, 27.57, 18.71, 18.68. **HRMS (ESI)** calculated [M+H]⁺ for C₂₁H₁₅O₄N₁F₃S: 418.0719, found: 418.0724. **FTIR (cm⁻¹)** 3440, 2924, 1761, 1672, 1517, 1451, 1391, 1147, 1077, 1047, 1012, 905.

(7*R*,7*aS*,11*aR*)-10-Methyl-7-((*E*)-styryl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-8-one (3v)

Following the general procedure, treatment of (*2E,4E*)-5-phenylpenta-2,4-dienal **2v** (59.3 mg, 0.375 mmol) and (*E*)-4-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1d** (70.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h

followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (*7R,7aS,11aR*)-10-methyl-7-((*E*)-styryl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-8-one **3v** as a white solid (101.0 mg, 93% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.35; er = 96:4, [α]_D²⁵ = 155.16 (c 1.0, CHCl₃). **HPLC** (ChiralpakAD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 10.6 min, *Major*: 13.0 min.

¹H NMR (400 MHz, CDCl₃) δ 8.23(d, *J* = 8.0 Hz, 1H), 8.06 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.29(s, 5H), 6.32 (dd, *J*₁ = 5.8 Hz, *J*₂ = 15.8 Hz, 2H), 6.16 (d, *J* = 15.6 Hz, 1H), 5.85 (s, 1H), 5.70 (d, *J* = 6.6 Hz, 1H) , 4.03 (t, *J* = 6.2 Hz, 1H), 3.37 (d, *J* = 6.3 Hz, 1H), 1.97(s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 174.53 (q, *J* = 35.2 Hz), 166.14, 149.39, 134.87 (q, *J* = 4.9 Hz), 133.96, 132.88, 131.66, 127.89, 125.88, 124.16, 124.14, 123.85, 120.53, 120.50, 120.18, 120.41, 116.08

(q, $J = 290.9$ Hz), 110.04, 101.05, 54.67, 42.55, 27.02, 17.76. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{19}O_3NF_3$: 438.1312, found: 438.1315. **FTIR (cm⁻¹)** 3435, 3027, 2924, 1762, 1670, 1516, 1451, 1392, 1148, 838.

(7*S*,7*aS*,11*aR*)-10-Cyclopropyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3w)

Following the general procedure, treatment of cinnamaldehyde **2a** (50.0 mg, 47 μ L, 0.375 mmol) and (*E*)-1-cyclopropyl-3-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)prop-2-en-1-one **1w** (76.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-10-cyclopropyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3w** as a white solid (104.0 mg, 95% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.50; er = 99:1, $[\alpha]_D^{25} = +146.6$ (c 0.1, $CHCl_3$). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 6.6 min, *Major*: 11.3 min.

¹H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, $J = 7.7$ Hz, 1H), 8.02 (s, 1H), 7.40-7.33 (m, 4H), 7.19 (d, $J = 7.2$ Hz, 1H), 6.84-6.82 (m, 2H), 6.34 (s, 1H), 5.69 (d, $J = 7.1$ Hz, 1H), 3.71 (t, $J = 6.5$ Hz, 1H), 3.41-3.39 (m, 1H), 1.57-1.52 (m, 1H), 0.74-0.72 (m, 1H). **¹³C NMR (100 MHz, $CDCl_3$)** δ 175.29 (q, $J = 35.3$ Hz), 167.41, 153.91, 138.79, 136.06, 133.36, 129.48, 128.86, 125.28, 124.86, 124.79, 121.69, 121.56, 121.35, 116.97 (q, $J = 291.0$ Hz), 111.15, 99.55, 57.30, 46.05, 27.03, 12.67, 5.13, 4.81. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{19}O_3N_1F_3$: 438.1312, found: 438.1318. **FTIR (cm⁻¹)** 2078, 1761, 1668, 1517, 1452, 1392, 1349, 1143, 1076, 967.

(7*S*,7*aS*,11*aR*)-10-Isobutyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3x)

Following the general procedure, treatment of cinnamaldehyde **2a** (40.0 mg, 38 μ L, 0.3 mmol) and (*E*)-5-methyl-1-(3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)hex-1-en-3-one **1x** (65.0 mg, 0.20 mmol) with triazolium salt **4** (11.0 mg, 0.03 mmol), oxidant **5** (123.0 mg, 0.3 mmol) and DABCO

(23.0 mg, 0.2 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford (7*S*,7*aS*,11*aR*)-10-isobutyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3x** as a white solid (69.0 mg, 76% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.60; er = 96:4, $[\alpha]_{\text{D}}^{25} = +113.5$ (c 0.2, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 7.7 min, *Major*: 9.9 min.

¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 1.1 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.35-7.33 (m, 3H), 7.19 (d, *J* = 7.4 Hz, 1H), 6.84 (dd, *J₁* = 6.6, *J₂* = 2.7 Hz, 1H), 6.36 (s, 1H), 5.67 (d, *J* = 7.1 Hz, 1H), 3.73 (t, *J* = 6.7 Hz, 1H), 3.38 (dd, *J₁* = 6.3, *J₂* = 1.8 Hz, 1H), 2.13-2.02 (m, 2H), 1.95-1.85 (m, 1H), 0.91 (dd, *J₁* = 13.4, *J₂* = 6.6 Hz, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.37 (q, *J* = 35.4 Hz), 167.64, 153.08, 138.93, 136.06 (q, *J* = 5.0 Hz), 133.42, 129.57, 128.93, 125.39, 124.89, 121.61, 121.54, 121.45, 117.0 (q, *J* = 291.0 Hz), 111.26, 102.70, 57.31, 45.99, 41.83, 27.08, 25.68, 22.41, 22.02. **HRMS (ESI)** calculated $[M+H]^+$ for C₂₆H₂₃O₃F₃N₁: 454.1625, found: 454.1630. **FTIR (cm⁻¹)** 3439, 2960, 1761, 1671, 1518, 1454, 1394, 1145, 1041, 907.

(7*S*,7*aS*,11*aR*)-2-Bromo-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3y)

Following the general procedure, treatment of cinnamaldehyde **2a** (50.0 mg, 47 μL, 0.375 mmol) and (*E*)-4-(5-bromo-3-(2,2,2-trifluoroacetyl)-1*H*-indol-7-yl)but-3-en-2-one **1y** (90.0 mg, 0.25 mmol) with triazolium salt **4** (15.0 mg, 0.037 mmol), oxidant **5** (153.0 mg, 0.375 mmol) and DABCO (28.0 mg, 0.25 mmol) in DMSO (2.0 mL) and stirring the reaction mixture at 25 °C for 12 h followed by flash column chromatography (Pet. ether- EtOAc: 9:1) to afford

(7*S*,7*aS*,11*aR*)-2-bromo-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one **3y** as a white solid (93.0 mg, 76% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.45; er = 99:1, $[\alpha]_{\text{D}}^{25} = +82.8$ (c 0.1, CHCl₃). **HPLC** (Chiralpak IA, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 10.4 min, *Major*: 8.5 min.

¹H NMR (400 MHz, CDCl₃) δ 8.50 (s, 1H), 8.09 (s, 1H), 7.42-7.34 (m, 5H), 6.87-6.85 (m, 2H), 6.43 (s, 1H), 5.71 (d, *J* = 7.1 Hz, 1H), 3.77 (t, *J* = 6.6 Hz, 1H), 3.49 (dd, *J₁* = 6.4, *J₂* = 1.8 Hz, 1H), 2.04 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.21 (q, *J* = 35.4 Hz), 167.13, 138.41,

136.48 (q, $J = 4.8$ Hz), 132.05, 129.63, 129.08, 126.16, 125.19, 124.92, 124.20, 123.09, 118.47, 116.82 (q, $J = 291.0$ Hz), 110.70, 101.17, 57.28, 45.70, 26.99, 18.78. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{16}O_3N_1F_3Br$: 490.0260, found: 490.0266. **FTIR (cm⁻¹)** 3436, 2924, 1764, 1674, 1516, 1451, 1394, 1306, 1147, 1045, 912.

7. Functionalization of Pyrroloquinolines

(4*S*,5*S*,6*R*)-Methyl 6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxylate (**6a**)

To a dry Schlenk tube containing compound **3a** (51.0 mg, 0.125 mmol) MeOH (2.0 mL) was added. The resulting mixture was allowed to stir overnight at 60 °C. Then the solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (5:1) to afford the (4*S*,5*S*,6*R*)-methyl 6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxylate **6a** (42.0 mg, 76% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.40; er = 95:5, $[\alpha]_D^{25} = +20.8$ (c 0.1, $CHCl_3$). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 6.4 min, *Major*: 8.0 min.

¹H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, $J = 7.9$ Hz, 1H), 7.56 (s, 1H), 7.42-7.41 (m, 3H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.18-7.16 (m, 3H), 5.64 (d, $J = 8.1$ Hz, 1H), 4.11 (s, 1H), 3.59 (dd, $J_1 = 8.6$, $J_2 = 4.3$ Hz, 1H), 3.52 (s, 3H), 3.16 (dd, $J_1 = 18.2$, $J_2 = 7.4$ Hz, 1H), 2.85 (d, $J = 15.0$ Hz, 1H), 2.15 (s, 3H). **¹³C NMR (100 MHz, $CDCl_3$)** δ 205.82, 175.18 (q, $J = 35.3$ Hz), 171.36, 135.15 (q, $J = 5.0$ Hz), 133.78, 129.57, 129.46, 125.09, 124.72, 124.29, 121.38, 121.30, 121.01, 116.96 (q, $J = 291.0$ Hz), 110.98, 58.90, 58.87, 52.39, 49.84, 49.79, 30.51, 29.87, 29.80. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{21}O_4N_1F_3$: 444.1417, found: 444.1427. **FTIR (cm⁻¹)** 3435, 2921, 1730, 1669, 1517, 1453, 1170, 997, 963.

(4*S*,5*S*,6*R*)-*N*-Benzyl-6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxamide (**7d**)

To a dry Schlenk tube containing compound **3a** (51.0 mg, 0.125 mmol) in THF (2.0 mL) was added benzylamine (28.0 μ L, 0.25 mmol) at room temperature. The resulting mixture was allowed to stir 48 h. Then the

solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the (4*S*,5*S*,6*R*)-*N*-benzyl-6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxamide **7d** (52.0 mg, 81% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.40; er = 97:3, [α]_D²⁵ = +28.7 (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 90:10 Hexane / IPA, 1.0 mL/min) *Minor*: 24.3 min, *Major*: 32.3 min.

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.48-7.13 (m, 10H), 6.67 (d, *J* = 5.6 Hz, 2H), 6.34 (s, 1H), 5.54 (t, *J* = 10.2 Hz, 1H), 4.37-4.23 (m, 2H), 3.94 (d, *J* = 12.8 Hz, 1H), 3.44 (dd, *J*₁ = 17.6, *J*₂ = 5.7 Hz, 1H), 3.26 (d, *J* = 6.7 Hz, 1H), 2.69-2.64 (m, 1H), 2.11 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 206.18, 169.97, 137.45, 136.47, 135.34, 135.30, 133.74, 129.62, 129.44, 128.60, 127.34, 127.07, 125.21, 124.72, 121.96, 120.86, 118.37, 115.48, 58.69, 51.90, 46.93, 43.20, 33.05, 30.57. **HRMS (ESI)** calculated [M+H]⁺ for C₃₀H₂₆O₃N₂F₃: 519.1890, found: 519.1898. **FTIR (cm⁻¹)** 3428, 2923, 1715, 1515, 1193, 1140, 1034, 996, 935.

(*E*)-Methyl 3-(7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*,8,11*a*-tetrahydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-3-yl)acrylate (8d**)⁶**

To a dry Schlenk tube containing compound **3a** (51.0 mg, 0.125 mmol), [RhCp*Cl₂]₂ (2.5 mol%), AgSbF₆ (10 mol%), acrylate derivative (0.5 mmol, 4 equiv) and Cu(OAc)₂·H₂O (0.125 mmol, 1equiv) and dichloroethane (1 mL). The Schlenk tube was placed in a pre-heated (100 °C) oil bath. After 6 h, the reaction mixture was cooled to room temperature, and diluted with diethyl ether and passed through a short silica gel (230-400 mesh size) bed, and repeatedly washed with diethyl ether (5 mL x 3 times). Then the solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (5:1) to afford the (*E*)-methyl 3-(7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*,8,11*a*-tetrahydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-3-yl)acrylate **8d** (49.0 mg, 79% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.40; er = 97:3, [α]_D²⁵ = -41.0 (c 0.1, CHCl₃). **HPLC** (Chiralcel OD, 80:20 Hexane / IPA, 1.0 mL/min) *Minor*: 34.3 min, *Major*: 38.3 min.

⁶ Lanke, V.; Bettadapur, K. R.; Prabhu, K. R. *Org. Lett.* **2016**, *18*, 5496.

¹H NMR (400 MHz, CDCl₃) δ 9.21 (d, *J* = 15.9 Hz, 1H), 8.12 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.33 (s, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 2H), 6.35 (d, *J* = 14.2 Hz, 2H), 5.66 (d, *J* = 6.9 Hz, 1H), 3.85 (s, 3H), 3.68 (t, *J* = 6.3 Hz, 1H), 3.41 (d, *J* = 6.3 Hz, 1H), 1.95 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 174.46 (q, *J* = 34.4 Hz), 167.54, 167.25, 150.79, 145.85, 138.75 (q, *J* = 5.4 Hz), 134.28, 129.63, 129.59, 125.22, 123.47, 123.30, 123.09, 122.32, 119.14, 117.48 (q, *J* = 291.0 Hz), 112.04, 101.57, 57.37, 51.85, 45.35, 27.09, 18.74. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₇H₂₀O₅N₁F₃Na: 518.1186, found: 518.1194. **FTIR (cm⁻¹)** 3442, 3140, 2924, 1765, 1633, 1404, 1349, 1286, 1187, 1147, 981, 955.

1-Benzyl-3-((7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)7,7*a*,8,11*a*-tetrahydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-3-yl)pyrrolidine-2,5-dione (9d**)⁷**

To a dry Schlenk tube containing compound **3d** (51.0 mg, 0.125 mmol), [RhCp*Cl₂]₂ (5.0 mol%), AgSbF₆ (20 mol%), *N*-benzyl maleimide (0.25 mmol, 2 equiv), AcOH (23 mg, 3 equiv) and AgOAc (63 mg, 3 equiv) and dichloroethane (1 mL). The Schlenk tube was placed in a pre-heated (120 °C) oil bath. After 12 h, the reaction mixture was cooled to room temperature, and diluted with diethyl ether and passed through a short silica gel (230-400 mesh size) bed, and repeatedly washed with diethyl ether (5 mL x 3 times). Then the solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (4:1) to afford the 1-benzyl-3-((7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)7,7*a*,8,11*a*-tetrahydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-3-yl)pyrrolidine-2,5-dione **9d** (61.0 mg, 81% yield) in 2:1 diastereomeric ratio (dr was determined by HPLC analysis).

R_f(Pet. ether /EtOAc = 70/30): 0.20; er = 95:5, [α]_D²⁵ = +116.4 (c 0.1, CHCl₃). **HPLC** (Chiralpak AD, 80:20 Hexane / IPA, 1.0 mL/min) *Minor*: 12.2 min, *Major*: 31.7 min, for another dr *Minor*: 21.4 min, *Major*: 25.2 min

¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.37-7.29 (m, 6H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.91-6.89 (m, 1H), 6.81-6.80 (m, 2H), 6.35 (s, 1H), 5.84 (bs, 1H), 5.63-5.59

⁷ Sherikar, M.S.; Kapaniaiah, R.; Lanke, V.; Prabhu, K. R. *Chem. Commun.* **2018**, 54, 11200.

(m, 1H), 4.79 (s, 1H), 3.66-3.61 (m, 1H), 3.48-3.36 (m, 2H), 2.70 (dd, $J_1 = 30.6$ Hz, $J_2 = 11.8$ Hz, 1H), 1.93 (s, 3H). **^{13}C NMR (100 MHz, CDCl_3)** δ 178.72, 176.26, 175.16 (q, $J = 34.4$ Hz), 167.04, 150.70, 138.99, 138.52, 136.18, 134.41, 132.74, 129.64, 129.07, 128.92, 128.86, 128.82, 128.81, 128.03, 125.27, 122.92, 121.12, 117.43 (q, $J = 291.0$ Hz), 111.65, 111.68, 101.53, 57.44, 45.32, 42.80, 39.69, 26.91, 18.72. Representative Peaks of Minor Isomer: **^{13}C NMR** δ 178.98, 176.20, 175.09 (q, $J = 34.3$ Hz), 167.36, 138.42, 136.17, 134.35, 101.73, 57.47, 44.95, 30.80, 26.83. **HRMS (ESI)** calculated $[\text{M}+\text{H}]^+$ for $\text{C}_{34}\text{H}_{26}\text{O}_5\text{N}_2\text{F}_3$: 599.1788, found: 599.1767. **FTIR (cm^{-1})** 1957, 1766, 1703, 1588, 1513, 1401, 1340, 1309, 1149, 1077, 970, 935, 755, 701, 630.

8. ^1H and ^{13}C NMR Spectra of Indole Derivatives

(*E*)-7-(3-Oxobut-1-en-1-yl)-1*H*-indole-3-carbaldehyde (**1c**)

(E)-4-(3-(2,2,2-Trifluoroacetyl)-1H-indol-7-yl)but-3-en-2-one (1d)

(E)-1-Cyclopropyl-3-(3-(2,2,2-trifluoroacetyl)-1H-indol-7-yl)prop-2-en-1-one (1w)

(E)-5-Methyl-1-(3-(2,2,2-trifluoroacetyl)-1H-indol-7-yl)hex-1-en-3-one (1x)

(E)-4-(5-Bromo-3-(2,2,2-trifluoroacetyl)-1H-indol-7-yl)but-3-en-2-one (1y)

9. ^1H and ^{13}C NMR Spectra of Pyrroloquinoline Derivatives

(7*S*,7*aS*,11*aR*)-10-Methyl-8-oxo-7-phenyl-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4-carbaldehyde (**3c**)

(7*S*,7*aS*,11*aR*)-10-Methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3d)

(7*S*,7*aS*,11*aR*)-7-(4-(Dimethylamino)phenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3e)

(7*S*,7*aS*,11*aR*)-7-(4-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one(3f)

7*S*,7*aS*,11*aR*)-10-methyl-7-(*p*-tolyl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3g)

(7*S*,7*aS*,11*aR*)-7-(4-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3h)

(7*S*,7*aS*,11*aR*)-7-(4-bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3i)

(7*S*,7*aS*,11*aR*)-10-Methyl-4-(2,2,2-trifluoroacetyl)-7-(4-(trifluoromethyl)phenyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3j)

Methyl 4-((7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*, 8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-7-yl)benzoate (3k)

(7*S*,7*aS*,11*aR*)-7-(3-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3I)

(7*S*,7*aS*,11*aR*)-7-(2-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*m*)

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*o*-tolyl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3n)

(7*S*,7*aS*,11*aR*)-7-(2-Fluorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3o)

(7*S*,7*aS*,11*aR*)-7-(2-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*p*)

(7*S*,7*aS*,11*aR*)-7-(3,4-Dichlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3q)

(7*S*,7*aS*,11*aR*)-7-(Benzo[d][1,3]dioxol-5-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3r)

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(naphthalen-2-yl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*s*)

(7*S*,7*aS*,11*aR*)-7-(Furan-2-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3t)

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(thiophen-2-yl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3u)

(7*R*,7*aS*,11*aR*)-10-Methyl-7-((*E*)-styryl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3v)

(7*S*,7*aS*,11*aR*)-10-Cyclopropyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3w)

(7*S*,7*aS*,11*aR*)-10-Isobutyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*x*)

(7*S*,7*aS*,11*aR*)-2-Bromo-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3y)

(4*S*,5*S*,6*R*)-Methyl 6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2-*ij*]quinoline-5-carboxylate (6d**)**

(4*S*,5*S*,6*R*)-N-Benzyl-6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2-*ij*]quinoline-5-carboxamide (7d)

(*E*)-Methyl 3-((7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*,8,11*a*-tetrahydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-3-yl)acrylate (8d**)**

1-Benzyl-3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)7,7a,8,11a-tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)pyrrolidine-2,5-dione (9d)

10. HPLC data of Pyrroloquinoline Derivatives

(7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-7-phenyl-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinoline-4-carbaldehyde (**3c**)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.556	MM	0.3594	982.03436	45.53738	23.4038
2	13.566	MM	0.4132	3214.00879	129.64984	76.5962

Sample Info : CHIRALPAK-AD, 20% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-10-Methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3d)

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(4-(Dimethylamino)phenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3e)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.359	MM	0.4296	2707.55664	105.05225	50.1092
2	14.503	MM	0.5947	2695.75757	75.55278	49.8908

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.301	MM	0.4424	6570.66162	247.52592	98.0508
2	14.561	MM	0.5431	130.62265	4.00854	1.9492

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(4-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3f)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.739	MM	0.2960	53.34007	3.00358	2.4888
2	13.976	MM	0.3600	2089.82959	96.76202	97.5112

Sample Info : CHIRALPAK-IA, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*p*-tolyl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*g*)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.987	MM	0.3785	6482.49805	285.48145	50.1788
2	10.194	MM	0.3977	6436.30127	269.70953	49.8212

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.932	MM	0.3629	653.18878	29.99679	3.7989
2	10.111	MM	0.4032	1.65408e4	683.73535	96.2011

Sample Info : CHIRALPAK-AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(4-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3h)

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(4-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3i)

Sample Info : CHIRALPAK-AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-10-Methyl-4-(2,2,2-trifluoroacetyl)-7-(4-(trifluoromethyl)phenyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3j)

Sample Info : CHIRALPAK-IA, 10% IPA-Hexane, 1.0 ml/min, 254nm

Methyl4-(7*S*,7*aS*,11*aR*)-10-methyl-8-oxo-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-7-yl)benzoate (3k)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.400	BB	0.6283	715.22528	17.48192	12.9786
2	20.373	MM	0.7821	4795.57080	102.19435	87.0214

Sample Info : CHIRALPAK -AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(3-Bromophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3l)

Sample Info : CHIRALPAK-IA, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(2-Methoxyphenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*m*)

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(*o*-tolyl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2-*ij*]quinolin-8(11*aH*)-one (3*n*)

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(2-Fluorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3o)

(7*S*,7*aS*,11*aR*)-7-(2-Chlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3p)

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(3,4-Dichlorophenyl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3q)

Sample Info : CHIRALPAK-IB, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(Benzo[d][1,3]dioxol-5-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3r)

Sample Info : CHIRALPAK-IA, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(naphthalen-2-yl)-4-(2,2,2-trifluoroacetyl)-7*a*,11*a*-dihydro-7*H*,8*H*-pyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8-one (3*s*)

Sample Info : CHIRALPAK-IA, 5% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-7-(Furan-2-yl)-10-methyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*t*)

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-10-Methyl-7-(thiophen-2-yl)-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3u)

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7R,7aS,11aR)-10-Methyl-7-((E)-styryl)-4-(2,2,2-trifluoroacetyl)-7a,11a-dihydro-7H,8H-pyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-8-one (3v)

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-10-Cyclopropyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3w)

Sample Info : CHIRALPAK AD, 10% IPA-Hexane, 1.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-10-Isobutyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7*a*-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3*x*)

Sample Info : CHIRALPAK AD 10% ipa-Hexane, 01.0 ml/min, 254nm

(7*S*,7*aS*,11*aR*)-2-Bromo-10-methyl-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7a-dihydropyrano[3,4-*c*]pyrrolo[3,2,1-*ij*]quinolin-8(11*aH*)-one (3y)

Sample Info : CHIRALPAK IA 10% ipa-Hexane, 1.0 ml/min, 254nm

(4*S*,5*S*,6*R*)-Methyl 6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxylate (6d)

Sample Info : CHIRALPAK AD 10% ipa-Hexane, 1.0 ml/min, 254nm

(4*S*,5*S*,6*R*)-N-Benzyl-6-(2-oxopropyl)-4-phenyl-1-(2,2,2-trifluoroacetyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carboxamide (7d)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.367	BB	0.9234	902.17737	14.96303	50.3240
2	36.006	BB	1.8065	890.56012	6.49168	49.6760

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.287	MM	1.0483	263.27377	4.18583	2.4661
2	32.388	BB	2.0575	1.04124e4	66.07457	97.5339

Sample Info : CHIRALPAK AD 10% ipa-Hexane, 1.0 ml/min, 254nm

(E)-Methyl 3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)-7,7a,8,11a-tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)acrylate (8d)

Sample Info : Chiralpakcel OD, 20% IPA-Hexane, 1.0 ml/min, 254nm

1-Benzyl-3-((7S,7aS,11aR)-10-methyl-8-oxo-7-phenyl-4-(2,2,2-trifluoroacetyl)7,7a,8,11a-tetrahydropyrano[3,4-c]pyrrolo[3,2,1-ij]quinolin-3-yl)pyrrolidine-2,5-dione (9d)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.086	BB	0.5280	5368.25928	152.76215	34.1754
2	20.995	MM	1.0116	2426.69727	39.98044	15.4489
3	24.973	MM	1.3115	2506.51416	31.85380	15.9570
4	31.695	BB	1.4347	5406.47070	57.30295	34.4187

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.218	MM	0.5485	507.62158	15.42547	3.2334
2	21.430	MM	1.0052	243.90909	4.04396	1.5536
3	25.286	MM	1.3092	4780.35254	60.85360	30.4493
4	31.735	MM	1.6709	1.01675e4	101.41505	64.7637

Sample Info : CHIRALPAK AD 20% ipa-Hexane, 1.0 ml/min, 254nm